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Analysis of equations of state for metals and rare gas solids

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A comparative study of different equations of state ... resented for some metals and rare gas solids It is shown that the Po... ...ima ...zuki and Shanker equa... ...of state are new approaches bu... they do not improve the results fo... ...mpression behavior although these ...ations required a lot of computation work The results obtained by Poi...ier-Tarantola sho... a significant improvement as compared with Suzuki and ...nker formalations The results obtained by Hama-Suito EOS are very ...igh The Tait EOS is found to give far better agreement with the available ...imental results than these new equations In the present study, the Ta...'s EOS is further extended to study the thermal expansion behavior of solids ...clusion of the concept of thermal pressure The new modified Tait's ...obaric EOS gives good agreement between calculated and experimental data ...h demonstrate the validity of the modified EOS

...words Equation of state metals rare gas solids, thermal pressure

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Introduction

...uation of state (EOS) is basically a relation between pressure, ...ume and temperature It has a very important role for analyzing thermophysical properties of different classes of solids The ...S is not only important in the basic and applied condensed ...tter physics but also in geophysics and earth and planetary ...ences There are many EOS's available in the literature [1-4] ...ny workers have proposed their EOS's on the basis of different ...s and continuous efforts are being made to formulate ...w EOS's Most of them are not capable to yield satisfactory ...ults at high pressure Many times the theories and equations ...state are very complicated, require many input parameter, ...ich are not always available and need very lengthy ...culations Besides these problems, the EOS's do not give ...d results Gaurav *et al* [5] reported the calculations using ...ne well-known EOS's without comparing the results with the ...erimental data Therefore, the study does not point out the ...eriority of any particular EOS In high-pressure, generally ...d theory is the finite strain theory, which means the theory ...e to Birch [6] The first equation based on potential which ...eived much attention was due to Morse [7] It was further improved by Rydberg [8] Vinet *et al* [9] have rediscovered the Rydberg potential as discussed by Stacey [3] There are some other formulations *viz* Suzuki formulation [10] based on Mie-Gruneisen theory, Shanker *et al* formulation [11] based on Gruneisen theory of thermal expansion

In present investigation, a comparative study is made by using different EOS's to identify the better equation of state that gives satisfactory agreement with the experimental data The Tait EOS [1,2] is also used to predict the compression in solids and the results are compared with that obtained by other EOS's in the light of experimental results It is found out that Tait's EOS gives better results The theory is further extended to study thermal expansion by applying the concept of thermal pressure [12-14] The thermal pressure (phonon pressure) in crystal is developed by the lattice vibration inside the crystals As the temperature increases, the amplitude of the vibration also increases, which enhances the thermal pressure of solids After inclusion of thermal pressure, the modified Tait isobaric EOS can not only predict the results close to experimental data but also requires less number of input parameters involving easy computational work In the present paper, we extend these studies for some important metals and rare gas solids to demonstrate the superiority of this EOS model

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The whole PVT (pressure, volume and temperature) surface of a solid can be predicted with the help of a universal EOS using a given set of data at zero pressure at a single reference temperature. The analysis of the behavior of hydrogen solid (n-H_2) is a rigorous test [15] for any universal EOS, because it is a highly compressible solid. Thus, relatively high values of compression (V/V_0) are reached although the applied pressure is not too high.

2. Method of analysis

The first quantum-based potential to receive serious attention was due to Morse [7]. The potential is based on the studies of molecular spectroscopy, which was used in a finite strain theory [6]. For many years, the Morse potential was the most favored equation for EOS studies. The potential gives the following form of the EOS [3]

$$P = 3K_0\left(x^{2/3} - x^{1/3}\right)\exp\left[\frac{3}{2}\left(K_0' - 1\right)\left(1 - x^{1/3}\right)\right], \tag{1}$$

where P is the pressure, K the bulk modulus, K' the pressure derivative of bulk modulus, $x = \rho/\rho_0 = V_0/V$ and $_0$ refers to their values at initial conditions.

Vinet *et al* [9,16,17] have obtained the following expression for pressure

$$P = 3K_0 y^{-2}(1 - y)\exp\left[\frac{3}{2}\left(K_0' - 1\right)\left(1 - x^{1/3}\right)\right] \tag{2}$$

In eq (2), $y = \left(V/V_0\right)^{1/3}$

Eqs (1) and (2) are the same. An excellent review on this subject has been written by Stacey [3].

Poirier-Tarantola EOS reads as follows [18]

$$P = K_0\frac{V_0}{V}\left[\ln\frac{V_0}{V} + \frac{\left(K_0' - 2\right)}{2}\left(\ln\frac{V_0}{V}\right)^2\right] \tag{3}$$

Hama-Suito EOS reads as follows [19]

$$P = 3K_0 x^{-5}(1 - x)\exp\left[\frac{3}{2}\left(K_0' - 3\right)(1 - x) + \left(A_2 - \frac{3}{2}\right)(1 - x)^2\right] \tag{4}$$

In eq (4), $x = \left(\frac{V_0}{V}\right)$

and $A_2 = \frac{3}{8}\left(K_0' - 1\right)\left(K_0' + 3\right) - \frac{3}{2}K_0K_0'' + \frac{1}{3}$

The EOS based on the Suzuki theory of thermal expansivity reads as follow [10,20]

$$P = K_0\left[\left(1 - \frac{V}{V_0}\right) + \left(\frac{K_0' - 1}{2}\right)\left(1 - \frac{V}{V_0}\right)^2\right]$$

The EOS based on Shanker formulation reads as follows [11]

$$P = K_0\left[\left(1 - \frac{V}{V_0}\right) + \left(\frac{K_0' + 1}{2}\right)\left(1 - \frac{V}{V_0}\right)^2\right]$$

The Tait's isothermal equation of state is given by the expression [1,2]

$$\frac{V}{V_0} = 1 - \frac{1}{K_0' + 1}\ln\left[1 + \frac{K_0' + 1}{K_0}P\right]$$

$$P = \frac{K_0}{A}\left[\left\{\exp A\left(1 - \frac{V}{V_0}\right)\right\} - 1\right]$$

Expanding the exponential term in eq (8) and neglecting the higher order terms, we get the following relation

$$P = K_0\left[\left(1 - \frac{V}{V_0}\right) + \left(\frac{K_0' + 1}{2}\right)\left(1 - \frac{V}{V_0}\right)^2\right]$$

Comparing eqs (5), (6) and (9), it is clear that eqs (6) and (9) are the same.

Now, the Tait EOS is modified by inclusion of thermal pressure. The thermal pressure P_{Th} is expressed as [12-14]

$$P_{Th} = \int_{T_0}^{T}\alpha_0 K_0 dT$$

Now, if thermal pressure is taken in account, then the effective pressure is reduced as

$$\frac{V}{V_0} = 1 - \frac{1}{K_0' + 1}\ln\left[1 + \frac{K_0' + 1}{K_0}\left(P - P_{Th}\right)\right]$$

On integrating above equation for thermal pressure and putting the value of thermal pressure, the equation can be expressed as

$$\frac{V}{V_0} = \left[1 - \frac{1}{K_0' + 1}\ln\left\{1 + \left(\frac{K_0' + 1}{K_0}\right)\left(P - \alpha_0K_0\left(T - T_0\right)\right)\right\}\right]$$

It may be considered that if the reference pressure is zero then this equation can be expressed as

$$\frac{V}{V_0} = \left[1 - \frac{1}{K_0' + 1}\ln\left\{1 - \left(K_0' + 1\right)\alpha_0\left(T - T_0\right)\right\}\right] \tag{10}$$

Eq (10) is the final modified Tait's equations of state, which ...mperature- dependent expression for thermal expansion in ...s It is also pointed out that the concept of thermal pressure also be applied on bulk modulus equation for obtaining ...perature- dependent equations of state

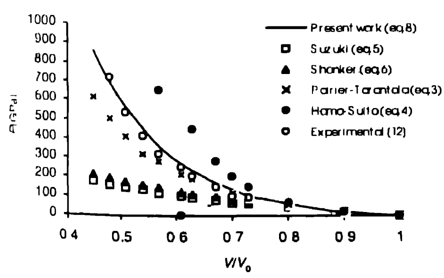
Results and discussion

... input parameters [5,15] required for present calculations ...compiled in Tables 1 We have selected four metals *viz* Cu, Pb ... and two rare gas solids *viz* Ar and Ne The choice of ...e materials depends on the availability of the experimental

...1 Input parameters [5,15] used in compression

Reference temperature (^{0}K)	K_0 in (GPa)	K_0'	K_0''	α_0 (in 10^{-5} K^{-1})
300	135	5 93	-0 083	5 04
300	72 6	4 85	-0 104	6 96
300	41 7	5 70	-	3 67
40	6 28	7 07	-2 52	106 8
60	6 36	7 61	2 86	60 0
294	11 55	3 51		13 98

...that the comparison can be made The results obtained ...compression behavior are shown in Figures 1-5 It is ...nd that the EOS based on the Suzuki formulation [eq (5)] ...es the results, which are very much low as compared with ...experimental data [20-23] The EOS based on the Shanker ...mulation [eq (6)] slightly improves the results of Suzuki but ...l there is a large deviation from the experimental data The ...of both these EOS's are improved by the EOS reported ...ier-Tarantola [eq (3)] The results obtained by the Hama-...to EOS [eq (4)] are very high as compared with the ...erimental data It is pertinent to mention here that Hama-...EOS needs the values of K_0'' which are rarely available in literature Perhaps Pb is such a case Therefore in the present ...er we are not using this EOS for Pb Eq (8) based on the ...rmodynamic analysis gives the results which are very much



...ure 1 Compression behaviour of copper using different EOS models

encouraging and compares well with the experimental data [20-23]. The percentage deviations calculated at the minimum value

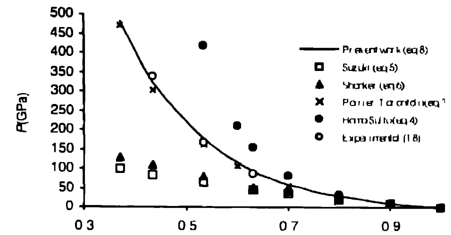


Figure 2 Compression behavior of aluminum using different EOS models

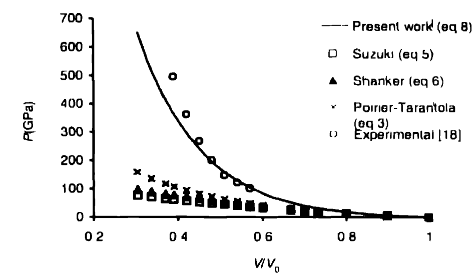


Figure 3. Compression behavior of lead using different EOS models

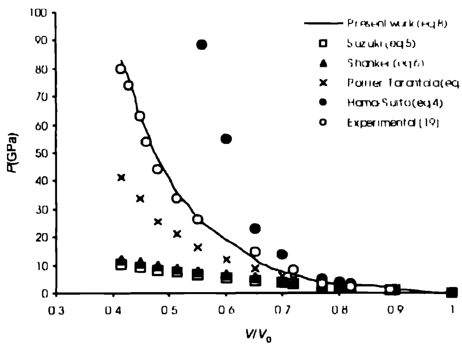


Figure 4. Compression behavior of argon using different EOS models

of V/V0 considered in the present work, are reported in Table 2 The similar trend of variation found for all the solids studied in the present work, demonstrates the better agreement by Tait's EOS

A good agreement obtained for the compression behavior of solids using eq (8), encouraged the authors to extend this

Table 2. Percentage deviations at minimum V/V_0 in compression

Solids	Percentage deviations				
	Present work (eq 8)	Suzuki (eq 5)	Shanker (eq 6)	Poirier-Tarantola (eq 3)	Hama Suito (eq 4)
Cu (at V/V_0=0.48)	3.3	77.8	72.8	30.0	390.3
Al (at V/V_0=0.37)	15.1	82.2	77.1	17.4	582.1
Pb (at V/V_0=0.30)	26.6	87.5	84.4	78.3	–
Ar (at V/V_0=0.41)	3.9	87.4	84.8	48.1	1968.7

model for the thermal expansion at P=0 Good agreement is also obtained for thermal expansion by using eq (10)

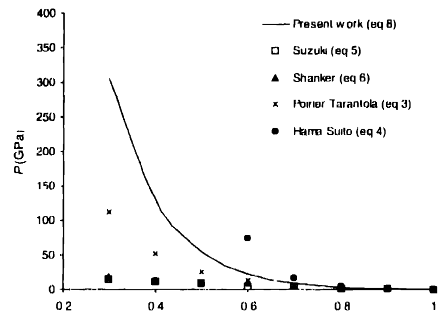


Figure 5 Compression behavior of neon using different EOS models

The results obtained using eq (10) are shown in Figures 6-8 for the Cu, Li and Ar. The experimental data [24,25] are readily available in the case of Cu, Li and Ar, which compare well with the present results Thus, a simple theory of thermal pressure seems to be applicable under high pressure and high temperature for the solids considered in the present work

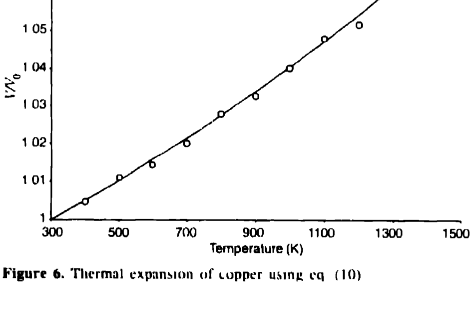


Figure 6. Thermal expansion of copper using eq (10)

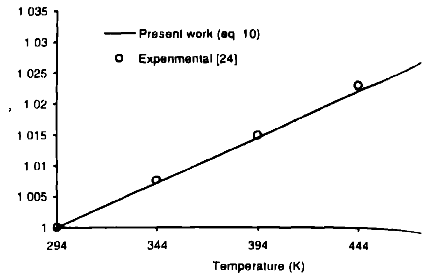


Figure 7. Thermal expansion of lithium using eq (10)

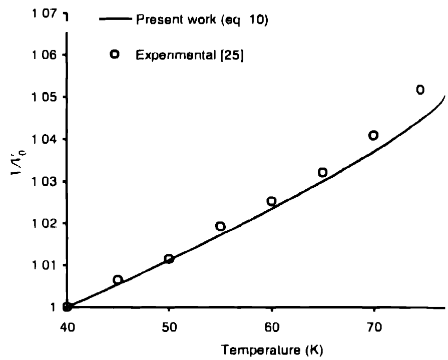


Figure 8. Thermal expansion of solid Ar from reference melting temperature using eq (10)

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